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(71) Applicant: **MURATA MFG CO LTD**

(72) Inventor: **HORIKAWA KATSUHIRO**

(54) **PRODUCTION OF PIEZOELECTRIC CERAMIC**

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a production process for piezoelectric ceramic elements that suppress the evaporation of Pb included in the piezoelectric material during the firing and can use an inexpensive metal as an electrode material.

SOLUTION: The production process for piezoelectric ceramic elements comprises the first step where at least individual oxides of Pb, Zr, Ti, Cr and Nb are mixed as the main to prepare their mixture; the second step where the mixture is fired to give the calcinated product; the third step where the calcinated product is crushed, Cu element is added thereto in an amount 0.05-3.0 wt.% calculated as CuO thereby obtaining an additive; the fourth step where a binder is added to the additive to form a binder mixture; the fifth step where the binder mixture is formed to formed products; the sixth step where the formed products are fired at a temperature of ≤1,100°C to prepare sintered products; and the seventh step where the electrodes are formed on the surface of the sintered products. The sintered product comprises the main component represented by the general formula: $Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$ (0.95≤d≤1.05; 0.40≤b≤0.55; 0.10≤x≤0.70; 0.02≤y≤0.12) and the sub-component of Cu in an amount of 0.05-3.0 wt.% calculated as CuO on the basis of the main component.

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(71)出願人　000006231
株式会社村田製作所
京都府長岡京市天神二丁目26番10号

(72)発明者　堀川　勝弘
京都府長岡京市天神二丁目26番10号　株式会社村田製作所内

(54)【発明の名称】　圧電セラミック素子の製造方法

(57)【要約】　　（修正有）

【課題】　焼成中において、圧電材料中に含有されているＰｂ蒸発量を抑制し、かつ電極材料に安価な金属を用いることができる圧電セラミック素子の製造方法。

【解決手段】　主成分として、少なくともＰｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂの各酸化物を含むように混合して混合物とする工程と、混合物を仮焼して仮焼物を得る工程と、仮焼物を粉砕し、Ｃｕ元素をＣｕＯに換算して０．０５～３．０重量%添加して添加物とする工程と、添加物にバインダーを加えてバインダー混合物とする工程と、バインダー混合物を成形して成形体とする工程と、成形体を１１００℃以下で焼成して焼結体とする工程と、焼結体の表面に電極を形成する工程とからなる圧電セラミック素子の製造方法であって、前記焼結体は、一般式：$Pb_a[(Cr_x Nb_{(1-x)})_y Zr_{(1-b-y)} Ti_b]O_3$で表される主成分に対して、副成分としてＣｕをＣｕＯに換算して、０．０５～３．０重量%含有してなる。

【特許請求の範囲】

【請求項１】（１）主成分として、少なくともＰｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂの各酸化物を含むように混合して混合物とする工程と、

（２）前記混合物を仮焼して仮焼物を得る工程と、

（３）前記仮焼物を粉砕し、Ｃｕ元素をＣｕＯに換算して０．０５～３．０重量％添加して添加物とする工程と、

（４）前記添加物にバインダーを加えてバインダー混合物とする工程と、

（５）前記バインダー混合物を成形して成形体とする工程と、

（６）前記成形体を１１００℃以下で焼成して焼結体とする工程と、

（７）前記焼結体の表面に電極を形成する工程と、からなる圧電セラミック素子の製造方法であって、

前記焼結体は、

一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$

（ただし、０．９５≦ａ≦１．０５

０．４０≦ｂ≦０．５５

０．１０≦ｘ≦０．７０

０．０２≦ｙ≦０．１２）で表される主成分に対して、副成分としてＣｕをＣｕＯに換算して、０．０５～３．０重量％含有してなることを特徴とする圧電セラミック素子の製造方法。

【請求項２】（１）主成分として、少なくともＰｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂの各酸化物を含むように混合して混合物とする工程と、

（２）前記混合物を仮焼して仮焼物とする工程と、

（３）前記仮焼物を粉砕し、Ｃｕ元素をＣｕＯに換算して０．０５～３．０重量％添加して添加物とする工程と、

（４）前記添加物にバインダーを加えてバインダー混合物とする工程と、

（５）前記バインダー混合物を成形してセラミックグリーンシートとする工程と、

（６）前記セラミックグリーンシートと、内部電極層とを交互に積層して積層体とする工程と、

（７）前記積層体を１１００℃以下の温度で焼成して焼結体とする工程と、

（８）前記焼結体上に外部電極を形成する工程と、からなる圧電セラミック素子の製造方法であって、

前記焼結体は、

一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$

（ただし、０．９５≦ａ≦１．０５

０．４０≦ｂ≦０．５５

０．１０≦ｘ≦０．７０

０．０２≦ｙ≦０．１２）で表される主成分に対して、

副成分としてＣｕをＣｕＯに換算して、０．０５～３．０重量％含有してなることを特徴とする圧電セラミック素子の製造方法。

【請求項３】　前記主成分中にＳｒ，Ｂａ，Ｃａ，Ｌａのうち少なくとも１種の元素からなる酸化物を添加し、かつ、その添加量が主成分中に含有されているＰｂ量の３．０mol％以下であることを特徴とする請求項１または請求項２に記載の圧電セラミック素子の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は積層圧電セラミック素子の製造方法に関する。

【０００２】

【従来の技術】従来より、Ｐｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂ，Ｏを含む圧電セラミック材料には、例えば、一般式：$Pb(CrNb)O_3-PbZrO_3-PbTiO_3$で表せる３成分系材料、およびこの３成分系材料に種々の微量添加物を添加した材料などが用いられている。これらの圧電体材料は、特公昭５１－２８３５８号公報、特開平８－３４６６７号公報に開示されているように、圧電特性が優れており、加工性や量産性も優れていることとから、圧電アクチュエータ、圧電フィルタ、圧電トランス、圧電センサ等に広く用いられている。

【０００３】また、近年、圧電応用装置に、圧電セラミック層と内部電極層を交互に積み重ねた積層型の圧電素子を用いるものが数多く開発されている。この積層型の圧電素子は、小型であり、かつ小電界で大きい変位が得られるというメリットがあるが、圧電セラミック層のセラミックグリーンシートと内部電極層とを共焼結させることが必要となる。したがって、焼結温度が１２００℃以上である上記のような圧電材料に使用できる内部電極材料としては、Ｐｔ等の高価な材料に限られている。そこで、過剰のＰｂＯを添加したり、SiO_2等のガラス成分を焼結助剤として添加し、焼結温度を低下させたりしている。

【０００４】

【発明が解決しようとする課題】しかしながら、従来の圧電セラミック素子の製造方法には、以下のような問題点があった。

【０００５】すなわち、圧電材料を焼結させるための焼成温度が１２００℃以上になる場合には、圧電材料中のＰｂの蒸発量が急激に増加する。このため、特性を一定に保つことが困難となる。

【０００６】また、１２００℃以下で圧電材料と内部電極層を共焼結させるために、SiO_2等のガラス成分を焼結助剤として添加した場合には、圧電材料の焼結温度は５０℃程度低下するものの、圧電特性が劣化してしまう。特に、大きな圧電特性が要求されるアクチュエータなどの圧電応用装置に用いることができない。

【０００７】本発明の目的は、焼成中において、圧電材

料中に含有されているPb蒸発量を抑制し、かつ圧電特性をほとんど劣化させることなく電極材料に安価な金属を用いることができる圧電セラミック素子の製造方法を提供することにある。

【0008】

【課題を解決するための手段】本発明は上記のような目的に鑑みてなされたものである。第1の発明の圧電セラミック素子の製造方法は、主成分として、少なくともPb，Zr，Ti，Cr，Nbの各酸化物を含むように混合して混合物とする工程と、前記混合物を仮焼して仮焼物を得る工程と、前記仮焼物を粉砕し、Cu元素をCuOに換算して0．05～3．0重量%添加して添加物とする工程と、前記添加物にバインダーを加えてバインダー混合物とする工程と、前記バインダー混合物を成形して成形体とする工程と、前記成形体を焼成して焼結体とする工程と、前記焼結体の表面に電極を形成する工程とからなる圧電セラミック素子の製造方法であって、前記焼結体は、一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$（ただし、0．95≦a≦1．05，0．40≦b≦0．55，0．10≦x≦0．70，0．02≦y≦0．12）で表される主成分に対して、副成分としてCuをCuOに換算して、0．05～3．0重量%含有してなることを特徴とする。

【0009】このような工程で圧電セラミック素子を製造することによって、焼結温度を低下させることができる。従って、焼成中に圧電材料中に含まれるPbの蒸発量を低く抑えることができるので、特性の安定化を図ることができる。また、圧電特性（圧電d定数、電気機械結合係数等）が大きい圧電セラミック素子とすることができる。

【0010】また、第2の発明の圧電セラミック素子の製造方法は、主成分として、少なくともPb，Zr，Ti，Cr，Nbの各酸化物を含むように混合して混合物とする工程と、前記混合物を仮焼して仮焼物とする工程と、前記仮焼物を粉砕し、Cu元素をCuOに換算して0．05～3．0重量%添加して添加物とする工程と、前記添加物にバインダーを加えてバインダー混合物とする工程と、前記バインダー混合物を成形してセラミックグリーンシートとする工程と、前記セラミックグリーンシートと、内部電極層とを交互に積層して積層体とする工程と、前記積層体を1100℃以下の温度で焼成して焼結体とする工程と、前記焼結体上に外部電極を形成する工程とからなる圧電セラミック素子の製造方法であって、前記焼結体は、一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$（ただし、0．95≦a≦1．05，0．40≦b≦0．55，0．10≦x≦0．70，0．02≦y≦0．12）で表される主成分に対して、副成分としてCuをCuOに換算して、0．05～3．0重量%含有してなることを特徴とする。

【0011】このような工程で圧電セラミック素子を製造することによって、焼成中に圧電材料中に含まれるPbの蒸発量を低く抑えることができるので、特性の安定化を図ることができる。また、圧電特性が大きい圧電セラミック素子とすることができる。さらに、圧電特性を圧電材料と共焼結させる内部電極層に銀やパラジウム等の安価な材料を用いることができ、圧電セラミック素子の製造コストを下げることができる。

【0012】また、第3の発明の圧電セラミック素子の製造方法においては、前記主成分中にSr，Ba，Ca，Laのうち少なくとも1種の元素からなる酸化物を添加し、かつ、その添加量が主成分中に含有されているPb量の3．0mol%以下であることが好ましい。

【0013】このような添加物を含有させることによって、圧電特性が大きい圧電材料であり、かつ圧電材料の焼結温度を1100℃以下とすることができる。

【0014】次に、本発明の圧電セラミック素子を実施例を用いてさらに具体的に説明する。

【0015】

【実施例】（実施例1）第1実施例である単板圧電セラミック素子の製造方法について説明する。図1は本実施例の単板圧電セラミック素子の概略斜視図を示す。まず、出発原料として、Pb_3O_4，ZrO_2，TiO_2，Cr_2O_3，Nb_2O_5をそれぞれ秤量し、4～32時間湿式混合して、$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$（以下、（Ⅰ）式とする）で表せる混合物を得た。次に、この混合物を脱水、乾燥させた後、800～1000℃の温度で2時間仮焼して仮焼物を得た。この仮焼物を粉砕した後、CuO粉末を添加し、さらに、PVA系バインダーを2～5重量%添加して、湿式混合および湿式粉砕を8～32時間行い、平均粒径が0．5～0．9μmのバインダー混合物を得た。このバインダー混合物を造粒後、1～1．5t／cm²の圧力でプレス成形し、直径が12mm、厚さが1．2mmの円板型成形体と、長辺が30mm、短辺が5mm、厚さが1．2mmの長方形型成形体との2種類の成形体を得た。次に、この成形体を1100℃以下で1～3時間焼成し、焼結体とした。さらに、図1のように、得られた焼結体2の両主面にAg電極ペーストを塗布し、800℃で0．5時間で焼き付けて電極3を形成した後、80～120℃の絶縁オイル中で、2．0～4．0kV／mmの直流電界を15～60分間印加して分極処理を施し、圧電セラミック素子1とした。

【0016】上記のようにして得られた圧電セラミック素子の主成分を構成する各元素のモル比を変動させ、電気的特性とキュリー点および抗折強度を測定した。なお、電気的特性は比誘電率εr、電気機械結合係数kp、圧電d定数d_{31}を測定した。このうち、電気機械結合係数と圧電d定数とをインピーダンスアナライザによる共振反共振法で評価し、さらに圧電d定数は変位測定により評価した。また、キュリー点は比誘電率εrの温

度変化の極大値をもって決定した。抗折強度は三点曲げ試験により評価した。なお、圧電ｄ定数と抗折強度には、長方形の素子を用い、その他は円板の素子を用いて測定した。その結果を表１に示す。なお、表中の※印は＊本発明の範囲外を示す。

【００１７】

【表１】

試料番号	$Pb_a[(Cr_xNb_{(1-x)})_bZr_{(1-b-y)}Ti_y]O_3$				CuO添加量(wt%)	焼成温度(℃)	電気的特性				抗折強度(Mpa)
	a	b	x	y			比誘電率 εr	電気機械係数 kp(%)	圧電d定数 d_{31} (pC/N)	キュリー点(℃)	
※1	0.92	0.44	0.33	0.06	1.75	1100	1134	56.3	−175	300	86
2	0.95	0.44	0.33	0.06	1.75	1100	1285	60.8	−210	310	93
3	0.98	0.44	0.33	0.06	1.75	1050	1403	63.5	−240	310	91
4	1.00	0.44	0.33	0.06	1.75	1050	1419	65.2	−250	310	88
5	1.02	0.44	0.33	0.06	1.75	1050	1487	64.2	−245	300	80
6	1.05	0.44	0.33	0.06	1.75	1050	1504	63.5	−240	310	72
※7	1.08	0.44	0.33	0.06	1.75	1050	1490	62.6	−225	300	60
※8	1.00	0.36	0.33	0.06	1.75	1050	610	55.7	−190	270	84
9	1.00	0.40	0.33	0.06	1.75	1050	1070	62.4	−225	280	87
10	1.00	0.48	0.33	0.06	1.75	1050	1780	66.2	−255	310	90
11	1.00	0.52	0.33	0.06	1.75	1050	1311	63.0	−220	320	93
12	1.00	0.55	0.33	0.06	1.75	1050	1034	60.3	−205	330	92
※13	1.00	0.58	0.33	0.06	1.75	1050	581	49.0	−160	350	85
14	1.00	0.48	0.10	0.06	1.50	1100	1956	65.9	−255	290	84
15	1.00	0.48	0.33	0.06	1.50	1100	1897	65.5	−250	310	96
16	1.00	0.48	0.50	0.06	1.50	1100	1425	63.4	−230	320	82
17	1.00	0.48	0.70	0.06	1.50	1100	1266	61.9	−215	320	77
※18	1.00	0.48	0.05	0.06	1.50	1100	2621	66.0	−260	290	88
※19	1.00	0.48	0.90	0.06	1.50	1100	987	58.5	−185	330	65
※20	1.00	0.44	0.00	0.00	2.00	1050	553	43.8	−135	320	58
21	1.00	0.44	0.33	0.02	2.00	1050	1096	60.0	−200	320	71
22	1.00	0.44	0.33	0.04	2.00	1050	1354	63.5	−230	310	83
23	1.00	0.44	0.33	0.06	2.00	1050	1380	64.1	−240	300	85
24	1.00	0.44	0.33	0.09	2.00	1050	1505	63.5	−230	280	80
25	1.00	0.44	0.33	0.12	2.00	1050	1676	62.0	−215	270	82
※26	1.00	0.44	0.33	0.15	2.00	1050	1712	59.0	−190	250	73
※27	1.00	0.44	0.33	0.06	0.00	1100	1620	58.8	−205	320	59
28	1.00	0.44	0.33	0.06	0.05	1100	1704	61.9	−220	320	72
29	1.00	0.44	0.33	0.06	1.00	1100	1546	62.5	−230	310	75
30	1.05	0.44	0.33	0.06	3.00	1000	1221	60.9	−220	310	78
※31	1.05	0.44	0.33	0.06	5.00	1000	822	51.7	−155	300	70

※印は本発明の範囲外

【００１８】表１に示すように、本発明の範囲内のものは、アクチュエータ等の応用圧電装置にも十分適用可能できる。なお、ここで応用圧電装置に適用可能であるとは、小電界の入力で大変位が得られ、応答速度が速いことである。すなわち、圧電特性がより大きく、比誘電率εｒがより小さいことであり、具体的には、電気機械係数ｋｐが６０％以上、圧電ｄ定数d_{31}が２００ｐＣ／Ｎ以上、比誘電率εｒが２０００以下のものである。また、リフロー半田付けに対応するためにキュリー点が２７０℃以上、使用時の大きな機械的応力に耐えるために抗折強度は７０ＭＰａ以上がそれぞれ必要である。

【００１９】ここで、実施例１を基に、請求項１および請求項２において、圧電セラミックの主成分の含有量を限定した理由を説明する。

（Ｉ）式中のａを０．９５≦ａ≦１．０５に限定したのは、試料番号１のように、ａが０．９５より小さい場合には、電気機械係数ｋｐが６０％より小さくなるうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり好ましくないからである。一方、試料番号７のように、ａが１．０５より大きい場合には、抗折強度が７０ＭＰａより小さくなり好ましくないからである。

【００２０】また、（Ｉ）式中のｂを０．４０≦ｂ≦０．５５に限定したのは、試料番号８のように、ｂが０．４０より小さい場合には、電気機械係数ｋｐが６０％より小さくなるうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり好ましくないからである。一方、試料番号１３のように、ｂが０．５５より大きい場合には、電気機械係数ｋｐが６０％より小さくな

るうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり好ましくないからである。

【００２１】また、（Ｉ）式中のｘを０．１０≦ｘ≦０．７０に限定したのは、試料番号１８のように、ｘが０．１０より小さい場合には、比誘電率εｒが２０００より大きくなり好ましくないからである。一方、試料番号１９のように、ｘが０．７０より大きい場合には、電気機械係数ｋｐが６０％より小さくなるうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり、さらに抗折強度が７０ＭＰａより小さくなり好ましくないからである。

【００２２】また、（Ｉ）式中のｙを０．０２≦ｙ≦０．１２に限定したのは、試料番号２０のように、ｙが０．０２より小さい場合には、電気機械係数ｋｐが６０％より小さくなるうえ、抗折強度が７０ＭＰａより小さくなり好ましくないからである。一方、試料番号２６のように、ｙが０．１２より大きい場合には、電気機械係数ｋｐが６０％より小さくなるうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり、さらにキュリー点が２７０℃より低くなり好ましくないからである。

【００２３】さらに、請求項１または請求項２において、副成分として添加するＣｕＯの添加量を主成分に対して０．０５～３．０重量％に限定したのは、試料番号２７のようにＣｕＯの添加量が０．０５重量％より少ない場合には、電気機械係数ｋｐが６０％より小さくなるうえ、抗折強度が７０ＭＰａより小さくなり好ましくない。一方、試料番号３１のように、ＣｕＯの添加量を３．０重量％より多い場合には、電気機械係数ｋｐが６０％より小さくなるうえ、圧電ｄ定数の絶対値｜d_{31}｜が２００ｐＣ／Ｎより小さくなり好ましくないからである。

【００２４】（実施例２）実施例１の試料番号２の焼成温度を変動させて、そのＰｂ蒸発量、電気的特性およびキュリー点を測定した。このうち、Ｐｂ蒸発量は蛍光Ｘ線定量分析法で測定し、その他は実施例１と同様にして測定した。その結果を図２に示す。

【００２５】図２に示すように、焼成温度が１１００℃を越えると主成分中のＰｂの蒸発量が急激に多くなることがわかる。主成分中のＰｂ量が少なくなると、電気機械係数ｋｐが小さくなったり、圧電ｄ定数の絶対値｜d_{31}｜が小さくなったりして特性上の問題が生じる。請求項１および請求項２において焼成温度を１１００℃以下としたのは、上記のような理由のためである。

【００２６】（実施例３）実施例１の試料番号２の主成分を混合する際に$SrCO_3$，$BaCO_3$，$CaCO_3$，$LaCO_3$から選ばれる少なくとも１種を添加し、主成分中のＰｂの含有量に対する上記添加物のモル比を変動させて電気的特性および抗折強度を測定した。その結果を表２に示す。なお、表中の＊印は請求項3における範囲外を示す。

【００２７】

【表２】

試料番号	添加元素				焼成温度 (℃)	電気的特性				抗折強度
	Sr (mol%)	Ba (mol%)	Ca (mol%)	La (mol%)		εｒ	kp (%)	d_{31} (pC/N)	キュリー点 (℃)	(Mpa)
41	1.0	0.0	0.0	0.0	1100	1334	63.2	−230	300	90
42	3.0	0.0	0.0	0.0	1100	1280	61.5	−210	280	78
＊43	5.0	0.0	0.0	0.0	1100	1057	55.6	−170	260	54
44	0.0	1.0	0.0	0.0	1100	1305	62	−210	300	85
45	0.0	3.0	0.0	0.0	1100	1163	60.4	−200	270	73
＊46	0.0	5.0	0.0	0.0	1100	958	53.1	−145	240	55
47	0.0	0.0	1.0	0.0	1100	1290	61.7	−215	300	83
48	0.0	0.0	3.0	0.0	1100	1186	60.2	−205	290	75
＊49	0.0	0.0	5.0	0.0	1100	1065	54.3	−150	280	60
50	0.0	0.0	0.0	1.0	1100	1658	63.8	−240	290	77
51	0.0	0.0	0.0	3.0	1100	1683	64.1	−240	270	72
＊52	0.0	0.0	0.0	5.0	1100	1195	58	−180	240	50
53	1.0	1.0	0.5	0.5	1100	1342	62.9	−225	280	78
＊54	2.0	1.0	1.0	1.0	1100	975	56	−160	250	58

＊印は請求項4の範囲外

【００２８】表２に示すように、上記４種の添加物のいずれを添加しても、圧電ｄ定数の絶対値、電気機械結合係数、キュリー点、抗折強度のいずれもが上記の基準をこえていることが確認できる。また、請求項３において、上記添加物の添加量を３．０重量％以下に限定したのは、試料番号４３，４６，４９，５２，５４のように、添加量が３．０重量％より多い場合には、比誘電率εｒは２０００以下であるものの、その他の電気的特性および抗折強度は、必要値以下もしくはその付近であり好ましくないからである。

【００２９】（実施例４）本実施例の積層圧電セラミック素子の製造方法について説明する。図３は本実施例の積層圧電セラミック素子の概略断面図である。まず、出発原料として、Pb_3O_4，ZrO_2，TiO_2，Ｃｒ

$_2O_3$，Nb_2O_5を表１の試料番号４，１０，１５と同組成となるようにそれぞれ秤量し、４～３２時間湿式混合して混合物を得た。次に、この混合物を脱水、乾燥させた後、８００～１０００℃の温度で２時間仮焼して仮焼物を得た。この仮焼物を粉砕した後、ＣｕＯ粉末を添加し、さらに、ＰＶＡ系バインダーを２～５重量％添加して、湿式混合および湿式粉砕を８～３２時間行い、平均粒径が０．５～０．９μｍのバインダー混合物を得た。このバインダー混合物を造粒後、ドクターブレード法で厚さ６０～１００μｍのセラミックグリーンシートを得た。次に、このセラミックグリーンシート上に、ＡｇとＰｄとの含有量比が７：３の内部電極ペーストを塗布して内部電極層を形成し、この内部電極層が交互に相対する面上に導出されるように、かつセラミックグリーンシートと内部電極層とが交互に積み重ねられるように積層し、積層体とした。次に、この成形体を１１００℃以下で１～３時間焼成し、圧電セラミック層と内部電極層とからなる積層焼結体とした。さらに、図３のように、外部電極ペーストを積層焼結体１２の上下の主面ほぼ全面に塗布し、８００℃で０．５時間焼き付けて第１外部電極１３ａを形成した。さらに、内部電極１４導出面である側面に導電ペーストを帯状に塗布して乾燥させ、第２外部電極１３ｂを形成した。このようにして外部電極１３を形成した積層焼結体１２を８０～１２０℃の絶縁オイル中で、２．０～４．０kV／mmの直流電界を１５～６０分間印加して分極処理を施して積層圧電セラミック素子１０とした。

【００３０】

【発明の効果】本発明の圧電セラミック素子の製造方法は、主成分として、少なくともＰｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂの各酸化物を含むように混合して混合物とする工程と、前記混合物を仮焼して仮焼物を得る工程と、前記仮焼物を粉砕し、Ｃｕ元素をＣｕＯに換算して０．０５～３．０重量％添加して添加物とする工程と、前記添加物にバインダーを加えてバインダー混合物とする工程と、前記バインダー混合物を成形して成形体とする工程と、前記成形体を焼成して焼結体とする工程と、前記焼結体の表面に電極を形成する工程とからなる圧電セラミック素子の製造方法であって、焼結体は、一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$（ただし、０．９５≦ａ≦１．０５，０．４０≦ｂ≦０．５５，０．１０≦ｘ≦０．７０，０．０２≦ｙ≦０．１２）で表される主成分に対して、副成分としてＣｕをＣｕＯに換算して、０．０５～３．０重量％含有してなる。

【００３１】また、主成分として、少なくともＰｂ，Ｚｒ，Ｔｉ，Ｃｒ，Ｎｂの各酸化物を含むように混合して混合物とする工程と、前記混合物を仮焼して仮焼物とする工程と、前記仮焼物を粉砕し、Ｃｕ元素をＣｕＯに換算して０．０５～３．０重量％添加して添加物とする工程と、前記添加物にバインダーを加えてバインダー混合物とする工程と、前記バインダー混合物を成形してセラミックグリーンシートとする工程と、前記セラミックグリーンシートと、内部電極層とを交互に積層して積層体とする工程と、前記積層体を１１００℃以下の温度で焼成して焼結体とする工程と、前記焼結体上に外部電極を形成する工程とからなる圧電セラミック素子の製造方法であって、前記焼結体は、一般式：$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$（ただし、０．９５≦ａ≦１．０５，０．４０≦ｂ≦０．５５，０．１０≦ｘ≦０．７０，０．０２≦ｙ≦０．１２）で表される主成分に対して、副成分としてＣｕをＣｕＯに換算して、０．０５～３．０重量％含有してなる。

【００３２】このような工程で圧電セラミック素子を製造するので、焼成時に主成分中のＰｂの蒸発量を抑えることができる。また、積層タイプのものの場合には、その内部電極にＡｇ，Ｐｄなどの安価な材料を用いることができる。さらに、圧電特性に優れた圧電セラミック素子とすることができる。

【図面の簡単な説明】

【図１】本発明にかかる実施例１である単板圧電セラミック素子の概略斜視図。

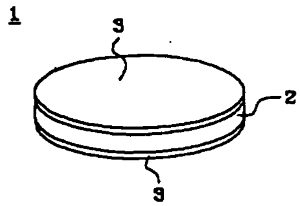
【図２】本発明の実施例２における試料の焼成温度とＰｂＯ蒸発量との関係を示すグラフ。

【図３】本発明にかかる実施例４である積層圧電セラミック素子の概略斜視図。

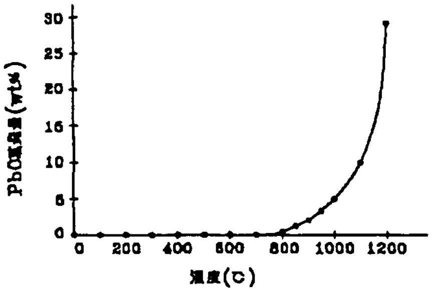
【符号の説明】

１	単板圧電セラミック素子
２，１２	焼結体
３	電極
１０	積層圧電セラミック素子
１３	外部電極
１４	内部電極

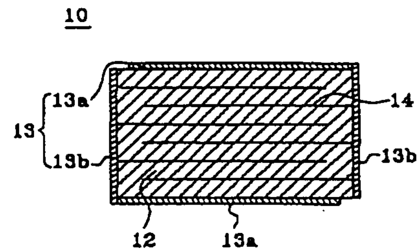
【図1】


1
3
2
3

【図2】


30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
温度(℃)

【図3】


10
13a
13
13b
14
13b
12
13a

(7)

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(71)Applicant :MURATA MFG CO LTD
(72)Inventor : HORIKAWA KATSUHIRO

(54) PRODUCTION OF PIEZOELECTRIC CERAMIC

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a production process for piezoelectric ceramic elements that suppress the evaporation of Pb included in the piezoelectric material during the firing and can use an inexpensive metal as an electrode material.
SOLUTION: The production process for piezoelectric ceramic elements comprises the first step where at least individual oxides of Pb, Zr, Ti, Cr and Nb are mixed as the main to prepare their mixture; the second step where the mixture is fired to give the calcinated product; the third step where the calcinated product is crushed, Cu element is added thereto in an amount 0.05-3.0 wt.% calculated as CuO thereby obtaining an additive; the fourth step where a binder is added to the additive to form a binder mixture; the fifth step where the binder mixture is formed to formed products; the sixth step where the formed products are fired at a temperature of <=1,100[deg]C to prepare sintered products; and the seventh step where the electrodes are formed on the surface of the sintered products. The sintered product comprises the main component represented by the general formula: Pba[(CrxNb(1-x))yZr(1-b-y)Tib]O3 (0.95<=d<=1.05; 0.40<=b<=0.55; 0.10<=x<=0.70; 0.02<=y<=0.12) and the sub-component of Cu in an amount of 0.05-3.0 wt.% calculated as CuO on the basis of the main component.

CLAIMS

[Claim(s)]
[Claim 1](1) The process which mixes as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, (2) -- the process which carries out temporary quenching of said mixture, and obtains a temporary-quenching object, and (3) -- with the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive(4) The process which adds a binder to said additive and is used as binder mixture, (5) -- the process which fabricates said binder mixture and is used as a Plastic solid, and (6) -- with the process which calcinates said Plastic solid below 1100 degrees C, and is used as a sintered compactIt is the manufacture approach of the becoming piezo-electric ceramic component. (7) -- the process which forms an electrode in the front face of said sintered compact -- since -- said sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] As opposed to the principal component expressed with O3 (however, 0.95<=a<=1.050.40<=b<=0.550.10<=x<=0.700.02<=y<=0.12)The manufacture approach of the piezo-electric ceramic component characterized by converting Cu into CuO as an accessory constituent, and coming to contain 0.05 to 3.0% of the weight.
[Claim 2](1) The process which mixes as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, (2) -- the process which carries out temporary quenching of said mixture, and is used as a temporary-quenching object, and (3) -- with the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive(4) The process which adds a binder to said additive and is used as binder mixture, (5) The process which fabricates said binder mixture and is used as a ceramic green sheet, (6) The process which carries out the laminating of said ceramic green sheet and the internal electrode layer by turns, and is made into a layered product, (7) The process which calcinates said layered product at the temperature of 1100 degrees C or less, and is used as a sintered compact, It is the manufacture approach of the becoming piezo-electric ceramic component. (8) -- the process which forms an external electrode on said sintered compact -- since -- said sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] As opposed to the principal component expressed with O3 (however, 0.95<=a<=1.050.40<=b<=0.550.10<=x<=0.700.02<=y<=0.12)The manufacture approach of the piezo-electric ceramic component characterized by converting Cu into CuO as an accessory constituent, and coming to contain 0.05 to 3.0% of the weight.

[Claim 3]The manufacture approach of the piezo-electric ceramic component according to claim 1 or 2 characterized by being less than [of the amount of Pb(s) which adds the oxide which consists of at least one sort of elements among Sr, Ba, calcium, and La into said principal component, and the addition contains in the principal component / 3.0mol%].

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacture approach of a laminating piezo-electricity ceramic component.
[0002]
[Description of the Prior Art]Conventionally, in the piezo-electric ceramic ingredient containing Pb, Zr, Ti, Cr, Nb, and O, it is a general formula :P The

ingredient which added various minute amount additives is used for 3 component system ingredient which can express with b(CrNb) O3-PbZrO3-PbTiO3, and this 3 component system ingredient. Since these piezo electric crystal ingredients are excellent in the piezo-electric property and workability and mass production nature are also excellent as indicated by JP,51-28358,B and JP,8-34667,A, they are widely used for the electrostrictive actuator, the piezo-electric filter, the piezoelectric transformer, the piezo-electric sensor, etc.

[0003] Moreover, many things using the piezoelectric device of the laminating mold which accumulated the piezo-electric ceramic layer and the internal electrode layer on piezo-electric application equipment by turns are developed in recent years. Although there is a merit that a large variation rate is obtained by this laminating type of piezoelectric device by small electric field small, it is needed to make the ceramic green sheet of a piezo-electric ceramic layer and an internal electrode layer co-sinter. Therefore, sintering temperature is restricted to expensive ingredients, such as Pt, as an internal electrode ingredient which can be used for the above piezoelectric material which is 1200 degrees C or more. Then, superfluous PbO is added, or the glass component of SiO2 grade is added as sintering acid, and sintering temperature is reduced.

[0004]

[Problem(s) to be Solved by the Invention] However, there were the following troubles in the manufacture approach of the conventional piezo-electric ceramic component.

[0005] That is, when the burning temperature for making piezoelectric material sinter becomes 1200 degrees C or more, the evaporation of Pb in piezoelectric material increases rapidly. For this reason, it becomes difficult to keep a property constant.

[0006] Moreover, although the sintering temperature of piezoelectric material falls by about 50 degrees C when the glass component of SiO2 grade is added as sintering acid in order to make piezoelectric material and an internal electrode layer co-sinter below 1200 degrees C, a piezo-electric property will deteriorate. It cannot use for piezo-electric application equipments, such as an actuator with which a piezo-electric big property is demanded especially.

[0007] The object of this invention is to offer the manufacture approach of a piezo-electric ceramic component that a cheap metal can be used for an electrode material, without controlling Pb evaporation contained in piezoelectric material during baking, and degrading most piezo-electric properties.

[0008]

[Means for Solving the Problem] This invention is made in view of the above objects. The manufacture approach of the piezo-electric ceramic component the 1st inventionThe process which mixes as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, The process which carries out temporary quenching of said mixture, and obtains a temporary-quenching object, and the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive, The process which adds a binder to said additive and is used as binder mixture, and the process which fabricates said binder mixture and is used as a Plastic solid, It is the manufacture approach of the piezo-electric ceramic component which consists of a process which calcinates said Plastic solid and is used as a sintered compact, and a process which forms an electrode in the front face of said sintered compact. Said sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] O3It is characterized by converting Cu into CuO as an accessory constituent, and coming to contain 0.05 to 3.0% of the weight to the principal component expressed with (0.95<=a<=1.05, 0.40<=b<=0.55, 0.10<=x<=0.70, 0.02<=y<=0.12). [however,]

[0009] Sintering temperature can be reduced by manufacturing a piezo-electric ceramic component at such a process. Therefore, since the evaporation of Pb contained in piezoelectric material during baking can be stopped low, stabilization of a property can be attained. Moreover, it can consider as a

piezo-electric ceramic component with piezo-electric large properties (piezo-electric d constant, electromechanical coupling coefficient, etc.).

[0010]Moreover, the manufacture approach of the piezo-electric ceramic component the 2nd inventionThe process which mixes as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, The process which carries out temporary quenching of said mixture, and is used as a temporary-quenching object, and the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive, The process which adds a binder to said additive and is used as binder mixture, and the process which fabricates said binder mixture and is used as a ceramic green sheet, The process which carries out the laminating of said ceramic green sheet and the internal electrode layer by turns, and is made into a layered product, It is the manufacture approach of the piezo-electric ceramic component which consists of a process which calcinates said layered product at the temperature of 1100 degrees C or less, and is used as a sintered compact, and a process which forms an external electrode on said sintered compact. Said sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] O3It is characterized by converting Cu into CuO as an accessory constituent, and coming to contain 0.05 to 3.0% of the weight to the principal component expressed with (0.95<=a<=1.05, 0.40<=b<=0.55, 0.10<=x<=0.70, 0.02<=y<=0.12). [however,]
[0011]Since the evaporation of Pb contained in piezoelectric material during baking by manufacturing a piezo-electric ceramic component at such a process can be stopped low, stabilization of a property can be attained. Moreover, it can consider as a piezo-electric ceramic component with a piezo-electric large property. Furthermore, cheap ingredients, such as silver and palladium, can be used for the internal electrode layer which makes a piezo-electric property co-sinter with piezoelectric material, and the manufacturing cost of a piezo-electric ceramic component can be lowered.
[0012]Moreover, in the manufacture approach of the piezo-electric ceramic component the 3rd invention, it is desirable that it is less than [of the amount of Pb(s) which adds the oxide which consists of at least one sort of elements among Sr, Ba, calcium, and La into said principal component, and the addition contains in the principal component / 3.0mol%].
[0013]By making such an additive contain, it is piezoelectric material with a piezo-electric large property, and sintering temperature of piezoelectric material can be made into 1100 degrees C or less.
[0014]Next, the piezo-electric ceramic component of this invention is explained still more concretely using an example.
[0015]
[Example](Example 1) The manufacture approach of the veneer piezo-electricity ceramic component which is the 1st example is explained. Drawing 1 shows the outline perspective view of the veneer piezo-electricity ceramic component of this example. First, as a start raw material, weighing capacity of Pb 3O4, ZrO2, TiO2 and Cr 2O3, and Nb2O5 was carried out, respectively, they carried out wet blending for 4 to 32 hours, and the mixture which can express with Pba[(CrxNb (1-x)) yZr(1-b-y) Tib] O3 (it considers as the (I) type hereafter) was obtained. Next, after dehydrating and drying this mixture, temporary quenching was carried out at the temperature of 800-1000 degrees C for 2 hours, and the temporary-quenching object was obtained. After grinding this temporary-quenching object, CuO powder was added, the PVA system binder was added further two to 5% of the weight, wet blending and wet grinding were performed for 8 to 32 hours, and the binder mixture whose mean diameter is 0.5-0.9 micrometers was obtained. After corning this binder mixture, press forming of the 1-1.5t /was carried out by the pressure of 3 cm, and the disk mold Plastic solid whose diameter is 12mm and whose thickness is 1.2mm, and the long side acquired two kinds of Plastic solids with the rectangle mold Plastic solid 5mm and whose thickness 30mm and a shorter side are 1.2mm. Next, this Plastic solid was calcinated below 1100

degrees C for 1 to 3 hours, and it considered as the sintered compact. Furthermore, after having applied Ag electrode paste to both the principal planes of the obtained sintered compact 2 like drawing 1, being burned at 800 degrees C in 0.5 hours and forming an electrode 3, in 80-120-degree C insulating oil, 2.0-4.0kV [/mm] direct-current electric field were impressed for 15 - 60 minutes, polarization processing was performed, and it considered as the piezo-electric ceramic component 1.

[0016]The mole ratic of each element which constitutes the principal component of the piezo-electric ceramic component obtained as mentioned above was fluctuated, and electrical characteristics, the Curie point, and anti-chip box reinforcement were measured. In addition, electrical characteristics measured specific-inductive-capacity epsilonr, the electromechanical coupling coefficient kp, and the piezo-electric d constant d31. Among these, the resonance antiresonance method by the impedance analyzer estimated the electromechanical coupling coefficient and piezo-electric d constant, and displacement measurement estimated piezo-electric d constant further. Moreover, the Curie point was determined with the maximal value of the temperature change of specific-inductive-capacity epsilonr. The three-point bending test estimated anti-chip box reinforcement. In addition, about piezo-electric d constant and anti-chip box reinforcement, others were measured using the component of a disk using the rectangular component. The result is shown in a table 1. In addition, * mark in a table shows the outside of the range of this invention.

[0017]
[A table 1]

試料番号	$Pb_a[(Cr_xNb_{(1-x)})_yZr_{(1-b-y)}Ti_b]O_3$				CuO添加量 (wt%)	焼成温度 (℃)	電気的特性				抗折強度 (Mpa)
	a	b	x	y			比誘電率 εr	電気機械係数 kp(%)	圧電d定数 d_{31} (pC/N)	キュリー点 (℃)	
※1	0.92	0.44	0.33	0.06	1.75	1100	1134	56.3	-175	300	86
2	0.95	0.44	0.33	0.06	1.75	1100	1285	60.8	-210	310	93
3	0.98	0.44	0.33	0.06	1.75	1050	1403	63.5	-240	310	91
4	1.00	0.44	0.33	0.06	1.75	1050	1419	65.2	-250	310	88
5	1.02	0.44	0.33	0.06	1.75	1050	1487	64.2	-245	300	80
6	1.05	0.44	0.33	0.06	1.75	1050	1504	63.5	-240	310	72
※7	1.08	0.44	0.33	0.06	1.75	1050	1490	62.6	-225	300	60
※8	1.00	0.36	0.33	0.06	1.75	1050	610	55.7	-190	270	84
9	1.00	0.40	0.33	0.06	1.75	1050	1070	62.4	-225	280	87
10	1.00	0.48	0.33	0.06	1.75	1050	1780	66.2	-255	310	90
11	1.00	0.52	0.33	0.06	1.75	1050	1311	63.0	-220	320	93
12	1.00	0.55	0.33	0.06	1.75	1050	1034	60.3	-205	330	92
※13	1.00	0.58	0.33	0.06	1.75	1050	581	49.0	-160	350	85
14	1.00	0.48	0.10	0.06	1.50	1100	1956	65.9	-255	290	84
15	1.00	0.48	0.33	0.06	1.50	1100	1897	65.5	-250	310	96
16	1.00	0.48	0.50	0.06	1.50	1100	1425	63.4	-230	320	82
17	1.00	0.48	0.70	0.06	1.50	1100	1266	61.9	-215	320	77
※18	1.00	0.48	0.05	0.06	1.50	1100	2621	66.0	-260	290	88
※19	1.00	0.48	0.90	0.06	1.50	1100	987	58.5	-185	330	65
※20	1.00	0.44	0.00	0.00	2.00	1050	553	43.8	-135	320	58
21	1.00	0.44	0.33	0.02	2.00	1050	1096	60.0	-200	320	71
22	1.00	0.44	0.33	0.04	2.00	1050	1354	63.5	-230	310	83
23	1.00	0.44	0.33	0.06	2.00	1050	1380	64.1	-240	300	85
24	1.00	0.44	0.33	0.09	2.00	1050	1505	63.5	-230	280	80
25	1.00	0.44	0.33	0.12	2.00	1050	1676	62.0	-215	270	82
※26	1.00	0.44	0.33	0.15	2.00	1050	1712	59.0	-190	250	73
※27	1.00	0.44	0.33	0.06	0.00	1100	1620	58.8	-205	320	59
28	1.00	0.44	0.33	0.06	0.05	1100	1704	61.9	-220	320	72
29	1.00	0.44	0.33	0.06	1.00	1100	1546	62.5	-230	310	75
30	1.05	0.44	0.33	0.06	3.00	1000	1221	60.9	-220	310	78
※31	1.05	0.44	0.33	0.06	5.00	1000	822	51.7	-155	300	70

※印は本発明の範囲外

[0018]As shown in a table 1, the thing of this invention within the limits can carry out application possible also to application piezoelectric devices, such as an actuator, enough. In addition, about is obtained [that it is applicable to an application piezoelectric device here, and] very much in the input of small electric field, and it is that a speed of response is quick. That is, it is that a piezo-electric property is more large and specific-inductive-capacity epsilonr is more small, and, specifically, for the electric machine multiplier kp, the piezo-electric d constant d31 is [200 or more pC/N and specific-inductive-capacity epsilonr] 2000 or less things 60% or more. Moreover, since it corresponds to reflow soldering, in order that the Curie point may bear the big mechanical stress at the time of 270 degrees C or more and an activity, 70 or more MPas are required for anti-chip box reinforcement respectively.

[0019]Here, in claim 1 and claim 2, the reason which limited the content of the principal component of a piezo-electric ceramic is explained based on an example 1.

(I) It is because having limited a in a formula to 0.95<=a<=1.05 does not become small and have absolute value |d31| of piezo-electric d constant in being smaller than 0.95 and a's becoming [the electric machine multiplier kp] smaller than 60% more desirable than 200 pC/N like a sample number 1. On the other hand, it is because a becomes [anti-chip box reinforcement] smaller than 70MPa(s) and is

not desirable when larger than 1.05 like a sample number 7.
[0020]Moreover, it is because having limited b in the (I) type to 0.40<=b<=0.55 does not become small and have absolute value |d31| of piezo-electric d constant in being smaller than 0.40 and b's becoming [the electric machine multiplier kp] smaller than 60% more desirable than 200 pC/N like a sample number 8. On the other hand, like a sample number 13, in being larger than 0.55 and b's becoming [the electric machine multiplier kp] smaller than 60%, it is because absolute value |d31| of piezo-electric d constant becomes small and is not more desirable than 200 pC/N.
[0021]Moreover, it is because having limited x in the (I) type to 0.10<=x<=0.70 does not become large and have specific-inductive-capacity epsilonr more desirable than 2000 like a sample number 18 when x is smaller than 0.10. On the other hand, like a sample number 19, when x is larger than 0.70, in the electric machine multiplier's kp becoming smaller than 60%, it is because absolute value |d31| of piezo-electric d constant becomes [become small and / anti-chip box reinforcement] smaller than 70MPa(s) further and is not more desirable than 200 pC/N.
[0022]Moreover, it is because it becomes [anti-chip box reinforcement in being smaller than 0.02 and y's becoming / the electric machine multiplier kp / smaller than 60%] smaller than 70MPa(s) and is not desirable like a sample number 20 to have limited y in the (I) type to 0.02<=y<=0.12. On the other hand, like a sample number 26, in being larger than 0.12 and y's becoming [the electric machine multiplier kp] smaller than 60%, it is because absolute value |d31| of piezo-electric d constant becomes small and the Curie point's becomes lower than 270 degrees C and is not still more desirable than 200 pC/N.

[0023]Furthermore, it becomes [anti-/ in the electric machine multiplier's kp becoming small 60% when there are few additions of CuO 0.05% of the weight like a sample number 27 in having limited the addition of CuO added as an accessory constituent in claim 1 or claim 2 to 0.05 - 3.0% of the weight to the principal component / chip box reinforcement] smaller than 70MPa(s) and is not desirable. On the other hand, like a sample number 31, in and the electric machine multiplier's kp becoming smaller than 60% about the addition of CuO than 3.0 % of the weight, it is because absolute value |d31| of piezo-electric d constant becomes small and is not more desirable than 200 pC/N.
[0024](Example 2) The burning temperature of the sample number 2 of an example 1 was fluctuated, and the Pb evaporation, electrical characteristics, and the Curie point were measured. Among these, Pb evaporation was measured by the fluorescence-X-rays quantitative-analysis method, and measured others like the example 1. The result is shown in drawing 2.
[0025]As shown in drawing 2, when burning temperature exceeds 1100 degrees C, it turns out that the evaporation of Pb in a principal component increases rapidly. If the amount of Pb(s) in a principal component decreases, the electric machine multiplier kp will become small, or absolute value |d31| of piezo-electric d constant will become small, and the problem on a property will arise. In claim 1 and claim 2, burning temperature was made into 1100 degrees C or less because [of the above reasons].
[0026](Example 3) When mixing the principal component of the sample number 2 of an example 1, at least one sort chosen from SrCO3, BaCO3, CaCO3, and LaCO3 was added, the mole ratio of the above-mentioned additive to the content of Pb in a principal component was fluctuated, and electrical characteristics and anti-chip box reinforcement were measured. The result is shown in a table 2. In addition, * mark in a table shows the outside of the range in claim 3.
[0027]
[A table 2]

試料番号	添加元素 Sr (mol%)	Ba (mol%)	Ca (mol%)	La (mol%)	焼成温度 (℃)	電気的特性 εr	kp (%)	d_{31} (pC/N)	キュリー点 (℃)	抗折強度 (Mpa)
41	1.0	0.0	0.0	0.0	1100	1334	63.2	-230	300	90
42	3.0	0.0	0.0	0.0	1100	1280	61.5	-210	280	78
*43	5.0	0.0	0.0	0.0	1100	1057	55.6	-170	260	54
44	0.0	1.0	0.0	0.0	1100	1305	62	-210	300	85
45	0.0	3.0	0.0	0.0	1100	1163	60.4	-200	270	73
*46	0.0	5.0	0.0	0.0	1100	958	53.1	-145	240	55
47	0.0	0.0	1.0	0.0	1100	1290	61.7	-215	300	83
48	0.0	0.0	3.0	0.0	1100	1186	60.2	-205	290	75
*49	0.0	0.0	5.0	0.0	1100	1065	54.3	-150	280	60
50	0.0	0.0	0.0	1.0	1100	1658	63.8	-240	290	77
51	0.0	0.0	0.0	3.0	1100	1683	64.1	-240	270	72
*52	0.0	0.0	0.0	5.0	1100	1195	58	-180	240	50
53	1.0	1.0	0.5	0.5	1100	1342	62.9	-225	280	78
*54	2.0	1.0	1.0	1.0	1100	975	56	-160	250	58

＊印は請求項4の範囲外

[0028]as shown in a table 2, even if it adds any of the four above-mentioned sorts of additives -- both the absolute value of piezo-electric d constant an electromechanical coupling coefficient the Curie point and anti-chip box reinforcement -- although -- it can check having surpassed the above-mentioned criteria. Moreover, in claim 3, like sample numbers 43, 46, 49, 52, and 54 in having limited the addition of the above-mentioned additive to 3.0 or less % of the weight, although specific-inductive-capacity epsilonr is 2000 or less when there are more additions than 3.0 % of the weight, other electrical characteristics and anti-chip box reinforcement are below a need value or its neighborhood, and it is because it is not desirable.

[0029](Example 4) The manufacture approach of the laminating piezo-electricity ceramic component of this example is explained. Drawing 3 is the outline sectional view of the laminating piezo-electricity ceramic component of this example. First, as a start raw material, weighing capacity was carried out, respectively, wet blending of Pb 3O4, ZrO2, TiO2 and Cr 2O3, and Nb2O5 was carried out for 4 to 32 hours so that it might become the sample numbers 4, 10, and 15 of a table 1, and this presentation, and mixture was obtained. Next, after dehydrating and drying this mixture, temporary quenching was carried out at the temperature of 800-1000 degrees C for 2 hours, and the temporary-quenching object was obtained. After grinding this temporary-quenching object, CuO powder was added, the PVA system binder was added further two to 5% of the weight, wet blending and wet grinding were performed for 8 to 32 hours, and the binder mixture whose mean diameter is 0.5-0.9 micrometers was obtained. The ceramic green sheet with a thickness of 60-100 micrometers was obtained with the doctor blade method after corning this binder mixture. Next, the laminating was carried out so that a ceramic green sheet and an internal electrode layer might be accumulated by turns, and it considered as the layered product so that the content ratio of Ag and Pd might apply the internal electrode paste of 7:3, an internal electrode layer might be formed on this ceramic green sheet and this internal electrode layer might be drawn on the field which faces by turns. Next, this Plastic solid was calcinated below 1100 degrees C for 1 to 3 hours, and it considered as the laminating sintered compact which consists of a piezo-electric ceramic layer and an internal electrode layer. furthermore, drawing 3 -- like -- **** of the upper and lower sides of external electrode paste of the laminating sintered compact 12 -- it applied to the whole surface mostly, it could be burned at 800 degrees C for 0.5 hours, and 1st external electrode 13a was formed. Furthermore, apply conductive paste to band-like, the side face which is an internal electrode 14 derivation side was made to dry it, and 2nd external electrode 13b was formed. Thus, 2.0-4.0kV [/mm] direct-current electric field were impressed for the laminating sintered compact 12 in which the external

electrode 13 was formed, for 15 - 60 minutes in 80-120-degree C insulating oil, polarization processing was performed, and it considered as the laminating piezo-electricity ceramic component 10.

[0030]

[Effect of the Invention] The process which mixes the manufacture approach of the piezo-electric ceramic component of this invention as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, The process which carries out temporary quenching of said mixture, and obtains a temporary-quenching object, and the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive, The process which adds a binder to said additive and is used as binder mixture, and the process which fabricates said binder mixture and is used as a Plastic solid, It is the manufacture approach of the piezo-electric ceramic component which consists of a process which calcinates said Plastic solid and is used as a sintered compact, and a process which forms an electrode in the front face of said sintered compact. A sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] O3To the principal component expressed with (0.95<=a<=1.05, 0.40<=b<=0.55, 0.10<=x<=0.70, 0.02<=y<=0.12), Cu is converted into CuO as an accessory constituent, and it comes to contain 0.05 to 3.0% of the weight. [however,]

[0031] Moreover, the process which mixes as a principal component so that each oxide of Pb, Zr, Ti, Cr, and Nb may be included at least, and is used as mixture, The process which carries out temporary quenching of said mixture, and is used as a temporary-quenching object, and the process which grinds said temporary-quenching object, converts Cu element into CuO, adds 0.05 to 3.0% of the weight, and is used as an additive, The process which adds a binder to said additive and is used as binder mixture, and the process which fabricates said binder mixture and is used as a ceramic green sheet, The process which carries out the laminating of said ceramic green sheet and the internal electrode layer by turns, and is made into a layered product, It is the manufacture approach of the piezo-electric ceramic component which consists of a process which calcinates said layered product at the temperature of 1100 degrees C or less, and is used as a sintered compact, and a process which forms an external electrode on said sintered compact. Said sintered compactGeneral formula :P ba [(CrxNb (1-x)) yZr(1-b-y) Tib] O3To the principal component expressed with (0.95<=a<=1.05, 0.40<=b<=0.55, 0.10<=x<=0.70, 0.02<=y<=0.12), Cu is converted into CuO as an accessory constituent, and it comes to contain 0.05 to 3.0% of the weight. [however,]

[0032] Since a piezo-electric ceramic component is manufactured at such a process, the evaporation of Pb in a principal component can be stopped at the time of baking. Moreover, in the case of a laminating type thing, cheap ingredients, such as Ag and Pd, can be used for the internal electrode. Furthermore, it can consider as the piezo-electric ceramic component excellent in the piezo-electric property.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The outline perspective view of the veneer piezo-electricity ceramic component which is the example 1 concerning this invention.

[Drawing 2] The graph which shows the relation of the burning temperature of a sample and PbO evaporation in the example 2 of this invention.

[Drawing 3] The outline perspective view of the laminating piezo-electricity ceramic component which is the example 4 concerning this invention.

[Description of Notations]

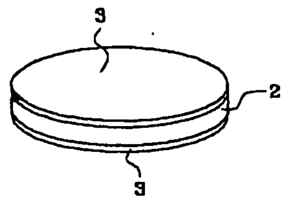
1 Veneer Piezo-electricity Ceramic Component

2 12 Sintered compact
3 Electrode
10 Laminating Piezo-electricity Ceramic Component
13 External Electrode
14 Internal Electrode

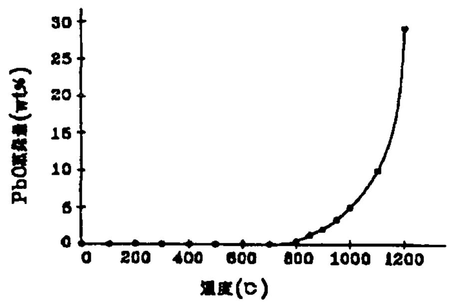
DRAWINGS

[Drawing 1]

1



[Drawing 2]



[Drawing 3]

10